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南海北部海盆区及邻近西太平洋黑潮区  
溶解有机物的光谱特性及调控因素

Optical Properties and Controlling Factors of Dissolved  
Organic Matter in the Basin of Northern South China Sea and  
the Adjacent Kuroshio Region

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## 摘 要

有色溶解有机物 (CDOM) 是海洋碳库的重要组成部分, 在海洋真光层内发生的光化学、光生物学过程中扮演着重要的角色, 同时也可用来示踪深海生物地球化学循环过程。南海是典型的大洋主控型边缘海, 其北部海盆区通过吕宋海峡与邻近的西太平洋黑潮区进行着活跃的物质和能量交换, 对整个南海及西太平洋碳的生物地球化学过程有着重要影响。但是, 利用 CDOM 的光谱指纹特征来示踪两个海区碳循环过程的研究还未见报道。本文在搭建海水低浓度 CDOM 吸收光谱测试系统的基础上, 结合三维荧光光谱测定与平行因子分析、主成分分析等手段, 系统研究了 2014 年 3~4 月南海北部海盆区及邻近西太平洋黑潮区 CDOM 的光谱特性及其空间分布规律, 并结合等密度混合模型、海表高度及表观耗氧量等参数, 讨论了黑潮水入侵对南海表层 CDOM 分布的影响, 对比了南海水与黑潮水两个端元 CDOM 的储量差异, 分析了中尺度过程和上升流对海洋真光层 CDOM 分布的影响, 探讨了真光层以下中、深层水体腐殖质组分的产生与积累, 初步构建了边缘海 CDOM 生物地球化学循环的基本框架。主要研究结果如下:

(1) 搭建了用于开阔大洋海水中低浓度 CDOM 吸收光谱测定的液芯波导系统, 规范了 CDOM 吸收光谱测试流程及液芯波导管路清洗维护方法, 提出了排除气泡干扰的经验措施, 完善了液芯波导系统测定海水 CDOM 吸收光谱的校正方法。对高浓度 CDOM 样品, 该方法的精密度优于 4%, 对 CDOM 含量极低的表层海水, CDOM 吸收系数及光谱斜率的相对标准偏差也 < 6.5%, 表明本文搭建的液芯波导系统在测定边缘海及开阔大洋海水 CDOM 吸收光谱上的稳定性和可靠性。

(2) 通过 PARAFAC 方法共鉴别出 5 种荧光组分, 包括 2 种类腐殖质荧光组分和 3 种类蛋白质荧光组分。水平分布上, 南海北部海盆区各荧光组分强度及吸收系数  $a_{350}$  均高于邻近黑潮区; 垂直分布上, 两个海区各组分垂直分布趋势均与开阔大洋区类似; 断面分布上, 南海北部海盆区真光层内 CDOM 局部分布特征明显受到中尺度涡和上升流的影响。南海北部海盆区及邻近西太平洋黑潮区 CDOM 主要来自海洋自生源和大洋本底信号, 没有陆源输入的影响。结合吕宋海峡中层水通量和两个海区中层水体 CDOM 的丰度差异, 计算得出南海北部海

盆中层水长波激发类腐殖质荧光组分 C1 向西太平洋的输出通量约为  $(2.89 \pm 1.70) \times 10^{11}$  R.U.m<sup>3</sup>/yr, 短波激发类腐殖质组分 C2 向西太平洋的输出通量为  $(1.71 \pm 0.33) \times 10^{11}$  R.U.m<sup>3</sup>/yr, CDOM 发色团的输出通量约为  $(1.13 \pm 0.28) \times 10^{13}$  m<sup>2</sup>/yr ( $a_{350}$ )。

(3) 春季南海北部海盆区黑潮入侵信号明显, 真光层内 2 个类腐殖质组分的分布主要受控于物理混合过程, 但类色氨酸组分的分布主要受控于生物活动, 而 CDOM 发色团的分布受物理混合和生物活动共同影响。根据等密度混合模型计算得知, 典型南海水端元上层 100m 水柱 CDOM 储量明显高于黑潮水端元, 其中 C2 组分的储量差值最大, 高达 82%, 类色氨酸组分的储量差值最小, 约为 23%, 不同组分储量差值的大小主要反映了光化学降解和生物活动产生两个过程综合作用的结果。此外, 南海北部海盆区活跃的中尺度涡对模型计算结果有显著影响, 暖涡会导致黑潮水比例 ( $R_k$ ) 计算值偏高, 冷涡则相反。

(4) 中层水体长波激发类腐殖质组分 C1 的荧光强度、吸收系数  $a_{350}$  与表观耗氧量 (AOU) 之间有着较为显著的正相关关系, 而短波激发类腐殖质组分 C2 与 AOI 之间的相关性不显著, 表明中层水 C1 组分生成速率明显高于 C2 组分, 且南海北部海盆区中层水 C1 组分、CDOM 发色团的产生速率略高于西太平洋黑潮区, 反映出两个海区颗粒有机物的输出通量差别。SEATS 站深层水中 C1、C2 组分存在明显的积累过程, 其产生速率分别为  $46.7 \times 10^{-5}$  R.U./( $\mu\text{mol/kg}$ )、 $29.7 \times 10^{-5}$  R.U./( $\mu\text{mol/kg}$ ), 与日本海深层水相当, 明显高于南海北部海盆中层水。

(5) 利用 C1、C2 两个类腐殖质组分生、消过程的差异, 本文构建了腐殖质比值指数 (CMR), 该指数不仅对南海北部海盆活跃的中尺度过程 (暖涡) 存在迅速的响应, 也可反映出不同水团的 CDOM 性质差异, 因此具有潜在的水团示踪意义。

**关键词:** 南海北部; 黑潮; 有色溶解有机物; 液芯波导; 中尺度涡; 腐殖质比值指数

## Abstract

Chromophoric dissolved organic matter (CDOM) is a ubiquitous component of the ocean carbon pool, and is important owing to its role in photochemical and photobiological processes, and its utility as a tracer of deep ocean biogeochemical circulation. Active matter and energy exchange between the basin of northern South China Sea (SCS) and the adjacent Kuroshio region of west Pacific Ocean occurs through the Luzon Strait, which is important for the carbon biogeochemistry of both sea areas. However, CDOM spectral characteristics has not been used as a tracer of carbon cycle process between the two regions. Based on the analytical system for measuring low abundance of sea water CDOM and the application of excitation-emission matrix fluorescence spectroscopy-parallel factor analysis and principal component analysis, the optical properties and spatial distribution pattern of CDOM in the basin of northern SCS and the adjacent Kuroshio region were systematically studied the influence of Kuroshio intrusion on the distribution of CDOM in the surface water of northern SCS were discussed using isopycnic mixing model, sea surface height and apparent oxygen utilization data. The differences of CDOM spectral features between the typical SCS and Kuroshio endmember were compared. The influence of mesoscale eddies and upwelling on the distribution of CDOM in the euphotic layer were also analyzed. In the intermediate and deep water below the euphotic layer, the production and accumulation of humic-like components were discussed. Finally, a preliminary mechanism of CDOM biogeochemical circulation in the ocean-dominated maginal sea was proposed. The main findings were:

(1) A liquid waveguide capillary cell (LWCC) system was set up to measure the absorption spectrum of CDOM in the open ocean. The analysis and cleaning procedures of absorption spectral analysis using this LWCC system were drawn up. The empirical measures to eliminate air bubble interference and the correction method for the determination of CDOM absorption spectra using the LWCC system were

proposed. The relative standard deviations of CDOM absorption coefficients and spectral slopes using such system were lower than 4% and 6.5% for the deep and surface water samples, respectively, demonstrating the stability and reliability of the established LWCC system in the determination of CDOM absorption spectra in the marginal sea and open ocean.

(2) Five fluorescent components were identified using PARAFAC model, including 2 humic-like and 3 protein-like components. The fluorescence intensities and absorption coefficients  $a_{350}$  of CDOM from the basin of northern SCS were lower than those from the adjacent Kuroshio region. The vertical distribution trend for each CDOM parameter in the two regions was similar. In the euphotic zone, local CDOM distribution in the basin of northern SCS was significantly affected by mesoscale eddies and upwelling. CDOM in the basin of northern SCS and the adjacent Kuroshio water mainly comes from primary production and oceanic background sources with little terrigenous input. Using the water flux via the Luzon Strait intermediate water and the difference of CDOM abundance in the two regions, the export flux of humic like components C1, C2 and CDOM chromophores were estimated as  $(2.89 \pm 1.70) \times 10^{11}$  R.U.m<sup>3</sup>/yr;  $(1.71 \pm 0.33) \times 10^{11}$  R.U.m<sup>3</sup>/yr and  $(1.13 \pm 0.28) \times 10^{13}$  m<sup>2</sup>/yr ( $a_{350}$ ), respectively.

(3) The signal of Kuroshio intrusion in the basin of northern SCS in spring of 2014 was obvious, which was revealed by the results of isopycnal mixing model. In the euphotic zone, the distribution of humic-like components C1 and C2 were mainly controlled by physical mixing process while the distribution of tryptophan-like component C4 was mainly controlled by biological activity. The distribution of CDOM chromophores was controlled by physical mixing and biological activity. CDOM inventory in the upper 100 m water column of the typical SCS water were higher than that of the typical Kuroshio water. The inventory of C2 component has the maximum difference (up to 82%) between the two end members, and such difference is small for component C4 (about 23%). Such difference in the CDOM properties for the two end members may be due to the different influence of the photochemical

degradation and biological activity on CDOM dynamics in two regions. In addition, active mesoscale eddies in the northern SCS basin can obviously affect the model results. Warm eddy will lead to the increase of the Kuroshio Water Ratio ( $R_k$ ) during the modelling, while for the cold eddy,  $R_k$  value will be lower than normal value.

(4) There was a significant positive correlation between fluorescence intensity of humic-like component C1, absorption coefficient ( $a_{350}$ ) and AOU in the intermediate water, but the relationship between C2 and AOU was very weak. This results showed that the production rate of component C1 was higher than that of component C2 in the intermediate water. The production rate of component C1 and CDOM chromophore in the basin of northern SCS was slightly higher than in the Kuroshio region of the west Pacific Ocean, reflecting the different degradation contribution of sinked particulate organic matter in the two regions. At SEATS station, components C1 and C2 showed apparent accumulation regime in the deep water, with the production rates of  $46.7 \times 10^{-5}$  R.U./( $\mu\text{mol kg}^{-1}$ ) and  $29.7 \times 10^{-5}$  R.U./( $\mu\text{mol kg}^{-1}$ ), respectively. These production rates were similar to those of the deep water of the Japan Sea, which was significantly higher than those of the intermediate water in the northern basin of the SCS.

(5) A new fluorescent index (C/M ratio, CMR) was proposed based on the difference in the process of production and degradation between the humic-like C1 (peak C) and C2 (peak M) components. CMR index can not only respond quickly to the active mesoscale processes (warm eddies) in the basin of NSCS, but also can reflect the CDOM characteristics between different water masses. Thus, CMR index can be utilized as a potential tracer for water mass movement in the open ocean.

**Key Words:** Northern South China Sea; Kuroshio; CDOM; LWCC; Mesoscale eddy; Humic-like ratio index (CMR)

## 缩略语表

DOM: 溶解有机物

CDOM: 有色溶解有机物

LWCC: 液芯波导

DOC: 溶解有机碳

EEMs: 激发-发射矩阵荧光光谱 (即三维荧光光谱)

PARAFAC: 平行因子分析

$a_{350}$ : 有色溶解有机物在波长 350 nm 处的吸收系数

$S_{275-295}$ : 波长范围在 275~295 nm 之间的光谱斜率

NPTW: 北太平洋热带水

NPIW: 北太平洋中层水

OceMar: 大洋主控型边缘海

CMR: 长波与短波类腐殖质组分荧光强度比值

ACE: 暖涡

CE: 冷涡



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